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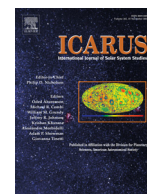
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Modelled isotopic fractionation and transient diffusive release of methane from potential subsurface sources on Mars



Adam H. Stevens^{a,b,*}, Manish R. Patel^{a,c}, Stephen R. Lewis^a

^a Department of Physical Sciences, The Open University, Milton Keynes, UK

^b UK Centre for Astrobiology, The University of Edinburgh, Edinburgh, UK

^c Space Science and Technology Division, Rutherford Appleton Laboratory, Harwell, Oxfordshire, UK

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ABSTRACT

We calculate transport timescales of martian methane and investigate the effect of potential release mechanisms into the atmosphere using a numerical model that includes both Fickian and Knudsen diffusion. The incorporation of Knudsen diffusion, which improves on a Fickian description of transport given the low permeability of the martian regolith, means that transport timescales from sources collocated with a putative martian water table are very long, up to several million martian years. Transport timescales also mean that any temporally varying source process, even in the shallow subsurface, would not result in a significant, observable variation in atmospheric methane concentration since changes resulting from small variations in flux would be rapidly obscured by atmospheric transport. This means that a short-lived 'plume' of methane, as detected by Mumma et al. (2009) and Webster et al. (2014), cannot be reconciled with diffusive transport from any reasonable depth and instead must invoke alternative processes such as fracturing or convective plumes.

It is shown that transport through the martian regolith will cause a significant change in the isotopic composition of the gas, meaning that methane release from depth will produce an isotopic signature in the atmosphere that could be significantly different than the source composition. The deeper the source, the greater the change, and the change in methane composition in both $\delta^{13}\text{C}$ and δD approaches -1000‰ for sources at a depth greater than around 1 km. This means that signatures of specific sources, in particular the methane produced by biogenesis that is generally depleted in $^{13}\text{CH}_4$ and CH_3D , could be obscured. We find that an abiogenic source of methane could therefore display an isotopic fractionation consistent with that expected for biogenic source processes if the source was at sufficient depth. The only unambiguous inference that can be made from measurements of methane isotopes alone is a measured $\delta^{13}\text{C}$ or δD close to zero or positive implies a shallow, abiogenic source. The effect of transport processes must therefore be carefully considered when attempting to identify the source of any methane observed by future missions, and the severe depletion in heavier isotopologues will have implications for the sensitivity requirements for future missions that aim to measure the isotopic fractionation of methane in the martian atmosphere.

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1. Introduction

Recent *in situ* measurements taken by the SAM instrument on the Mars Science Laboratory confirm the existence of temporally variable martian methane (Krasnopolsky et al., 2004; Mumma et al., 2009; Webster et al., 2014). A number of sources have been proposed to explain the presence of methane on Mars, including biogenesis (Summers et al., 2002), serpentinisation of mafic

rocks in the crust (Oze and Sharma, 2005), or the destabilisation of methane clathrate hydrate (MCH) deposits in the cryosphere (Chastain and Chevrier, 2007), but determining which of these is responsible is a difficult task.

The source processes mentioned above all occur in the subsurface and so any methane must be transported through the martian regolith before entering the atmosphere, where it can be observed via spectroscopy and other techniques. In the cases of the deeper sources such as serpentinisation or methanogenesis, which both require liquid water (Oze and Sharma, 2005; Tosca et al., 2008), this transport would be through several kilometres of regolith. In the case of release from methane clathrate hydrate (MCH) deposits,

* Corresponding author.

E-mail address: adam.stevens@ed.ac.uk (A.H. Stevens).

it may be only metres to hundreds of metres (Elwood Madden et al., 2011). Understanding how the transport of gas through the martian regolith affects the properties of methane may provide one piece of the puzzle in helping to identify the sources of this gas.

Previous research investigating the transport of gases through martian regolith was reviewed in Stevens et al. (2015), who proposed a numerical model for gas transport through the martian subsurface based on Fickian diffusion. Here we improve on this model by incorporating the full Dusty Gas Model (DGM) of gas transport through porous media. The DGM accounts for Knudsen diffusion, which is more applicable to the low permeability environment of the deep martian subsurface (Fen and Abriola, 2004).

This improved model is then used to investigate how the isotopic fractionation of observed methane will be affected by transport. The model calculates the isotopic composition at the surface as release occurs, and determines the difference between the isotopic composition at the source and at the surface. Using these results with future observations of the isotopic fractionation of martian methane will allow some aspects of the source to be constrained.

1.1. Transport in porous media

In general, the Advective Diffusive Model (ADM) of fluid transport, which is based purely upon Fickian diffusion, produces good results for media with high permeability, but deviates from observations of media with low permeability, where Knudsen-type diffusion (molecule-wall interactions dominating over molecule-molecule interactions) has an increased role (Ho and Webb, 2006). Given that the martian regolith is likely to be very low permeability at depth (Clifford, 1993), the ADM is unlikely to be applicable to a full range of martian subsurface environments. The DGM includes the porous medium as a component in diffusion as a ‘dusty gas’ and includes coupling between ordinary diffusion, Knudsen diffusion, and advection (Webb and Pruess, 2003).

In the limit of considering a trace gas (where the mass fraction of the trace gas, ω_1 , is negligible compared to the main carrier gas, ω_2), the DGM gives the diffusive flux (in one dimension) as

$$J = -\frac{D_{1K}}{D_z + D_{1K}} D_z \rho \frac{\partial \omega_1}{\partial z} - \frac{D_{1K}(D_z + D_{2K})}{D_z + D_{1K}} \rho \omega_1 \frac{1}{P} \frac{\partial P}{\partial z} \quad (1)$$

where J is the mass flux, D_z is the effective diffusivity, D_{iK} is the Knudsen diffusivity of species i , ρ is the gas density, P is the total pressure and ω_1 is the mass fraction of the trace gas (Webb and Pruess, 2003). The first term accounts for diffusion and the second for advectively coupled diffusion. In the case where $D_{1K} \gg D_z$ (which will occur at high permeability) and where there is no pressure gradient, this relation reduces directly to Fick’s law.

A Fickian model that incorporates Knudsen diffusion is only sufficient in cases where pressure gradient effects are not important (Sleep, 1998). The DGM is the most rigorous available description of the subsurface transport of gas (Fen and Abriola, 2004), but adds significant complexity over the ADM.

1.2. Effects of transport

Diffusive and advective transport mechanisms affect molecular isotopologues to a different extent, because the free diffusion coefficient, D_{12} , and the Knudsen diffusion coefficient, D_{1K} , depend on the molecular mass (M) of the gas species in question, which varies between isotopologues. This means that any diffusive transport will change the isotopic composition of a gas from its value at the source of the gas, which could therefore obscure a particular isotopic signature that would otherwise identify the source process. Using isotopic fractionation to identify source and sink

processes has been extensively investigated for terrestrial applications with natural gases, using a variety of transport and reaction models and both field and laboratory measurements. This method therefore has extensive heritage.

Zhang and Krooss (2001) measured the diffusion of methane through water-saturated shales to understand how the presence of organic carbon in the rock affects the fractionation. They observed depletion of heavier methane ($^{13}\text{CH}_4$) compared to the source gas that was dependent on diffusion time, with values between -60 and -40% compared to an original source of -39.1% .

De Visscher et al. (2004) calculated the difference between the diffusion constants of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ from theoretical considerations, finding that

$$\frac{D_{^{12}\text{CH}_4}}{D_{^{13}\text{CH}_4}} = 1.0195 \quad (2)$$

and found the measured value from experiment to be 1.0178 ± 0.0009 but offer no comment as to the reason for the difference, though they neglected to take Knudsen diffusion into account.

Trudinger et al. (1997) used a finite difference model to calculate an “isotopic diffusion correction” value that included the relative effects of diffusive and gravitational fractionation. They used this depth-dependent correction value, of around a few parts *per mille*, to reconstruct historical isotopic records from ice cores and so reproduce the isotopic ratio of the Earth’s past atmosphere. They show that the isotopic fractionation measured in ice cores is different from the emplaced value due to diffusion through upper layers of snow.

To date, the effect of fractionation during gas transport through the martian subsurface has not been investigated. A transport model can be used to estimate the isotopic composition of gas observed in the atmosphere compared to that of the original source. This information, along with measurements of the isotopic fractionation in the atmosphere could be used to place constraints upon which of these possible sources produced the gas that is observed.

2. Model description

For a region of a porous medium with porosity ϕ , mass conservation implies that for a gas with a density, ρ , and mass fraction of ω in that region and a total net flux of the same gas J ,

$$\frac{\partial \phi \rho \omega}{\partial t} + \frac{\partial J}{\partial z} = 0 \quad (3)$$

substituting the DGM flux (Eq. 1) gives

$$\frac{\partial \phi \rho \omega}{\partial t} = \frac{\partial}{\partial z} \left(\frac{D_{1K}}{D_z + D_{1K}} D_z \rho \frac{\partial \omega_1}{\partial z} \right) + \frac{\partial}{\partial z} \left(\frac{D_{1K}(D_z + D_{2K})}{D_z + D_{1K}} \rho \omega_1 \frac{1}{P} \frac{\partial P}{\partial z} \right) \quad (4)$$

This can be solved using the Crank-Nicolson finite difference method with an evenly spaced grid. The boundary conditions of the system use a constant zero value condition in the layer of atmosphere above the top of the regolith column to simulate the effect of having a well-mixed atmosphere above that moves diffused gas away at timescales shorter than the diffusion from the surface, shown to be valid by Stevens et al. (2015). The resulting Crank-Nicolson matrices are more complex than those representing ADM transport, but due to their tridiagonal nature can be solved without significant added computational complexity. This then allows for simulation of the transport of trace gases through a porous martian regolith.

The Fickian diffusion coefficient, D_{12} , is modified with an “obstruction factor” that incorporates some of the properties of the

medium itself (Hudson et al., 2007). The ‘effective diffusivity’ for a porous medium is defined as

$$D_z = \frac{\phi(z)}{\tau(z)} D_{12} \left(\frac{T(z)}{T_{\text{ref}}} \right)^{3/2} \frac{P_{\text{ref}}}{P(z)} \quad (5)$$

where $\phi(z)$, $\tau(z)$, $T(z)$ and $P(z)$ are the porosity, tortuosity, temperature and pressure at a given depth, D_{12} is the free gas diffusivity of gas 1 in gas 2, and T_{ref} and P_{ref} are a reference temperature and pressure for a given gas.

The Knudsen diffusivity can be determined by the Klinkenberg coefficient, b_i , the fluid viscosity, μ , and the permeability of the medium, k , using (Ho and Webb, 2006)

$$D_{ik} = \frac{kb_i}{\mu_i} \quad (6)$$

The Klinkenberg coefficient for a given gas with molecular mass, m , at a given temperature, T , is given by

$$b_i = b_{\text{ref}} \left(\frac{\mu_i}{\mu_{\text{ref}}} \right) \left(\frac{m_{\text{ref}}}{m_i} \right)^{1/2} \left(\frac{T_i}{T_{\text{ref}}} \right)^{1/2} \quad (7)$$

where b_{ref} is an experimentally derived reference parameter for a given gas at the conditions indicated by subscript ‘ref’ parameters, in this case for nitrogen at STP (Thorstenson and Pollock, 1989).

In order to track the isotopic composition of the gas during transport, more than one species must be modelled at the same time. Here the assumption is made that the isotopologues of methane do not interact in a significant way. The molecular masses of CH_4 , $^{13}\text{CH}_4$ and CH_3D are 16.0425, 17.0351 and 17.0486 Da respectively. The differing molecular mass of the isotopologues means that their molecule-specific diffusivity and Knudsen diffusivity values (D_{12} and D_K) are different. The mass dependence of D_{12} as given by Marrero and Mason (1972) means (assuming the change in the size of the molecule is negligible) that

$$D_{ij} \propto \sqrt{\frac{M_i + M_j}{M_j}} \quad (8)$$

and therefore the relative diffusivity is given by

$$\frac{D_{ij}}{D_{kl}} = \sqrt{\frac{M_l}{M_j} \frac{M_i + M_j}{M_k + M_l}} \quad (9)$$

meaning it is possible to calculate the relative diffusivity of two species just based on their molecular mass, M . Following this,

$$D_{^{13}\text{CH}_4-\text{CO}_2} = D_{^{12}\text{CH}_4-\text{CO}_2} \times 1.0195 \quad (10)$$

and

$$D_{\text{CH}_3\text{D}-\text{CO}_2} = D_{^{12}\text{CH}_4-\text{CO}_2} \times 1.0083 \quad (11)$$

The Knudsen diffusivity also depends on the molecular mass, and also scales as the square root of the ratio of masses. Any changes to the viscosity or density of the bulk gas due to varying composition of each isotopologue are assumed to be negligible.

The model does not include adsorptive fractionation, which could have a strong effect on gas transport through the highly porous martian regolith. The process of adsorption creates a strong negative fractionation in the gas around the adsorbing surfaces (Prinzhofer and Pernaton, 1997). Experiments simulating the cold, high surface area environment of the martian regolith have shown that adsorption can have a significant instantaneous effect on methane transport (Gough et al., 2010) but it remains unclear what the net effect will be, given that an adsorptive equilibrium will likely be reached rapidly (Meslin et al., 2011), which would only be disrupted by temperature changes at depths far greater than the thermal skin-depth of the martian regolith (Mellon and Jakosky, 1993).

Another potentially major influence would be where methane was confined, perhaps due to overlying ice blocking pore space, increasing the local pressure. If the confining conditions were removed, perhaps due to similar mass-wasting events or faulting, this high pressure volume of methane would be transported much more rapidly than in the case of diffusion alone. Release from such a high-pressure reservoir would quickly reduce the pressure gradient, but such a situation could generate short-lived ‘plumes’ of methane; however this process is beyond the scope of this work, especially given the large uncertainties in martian subsurface conditions.

2.1. Simulating the regolith column

The properties of the regolith column used in the model are calculated in the same manner as in Stevens et al. (2015) in order to provide direct comparison, to which the reader is referred for a discussion of the issues with modelling the martian subsurface and current unknowns.

The subsurface porosity and tortuosity at depth z are given by

$$\phi(z) = \phi_0 e^{(-\frac{z}{K})} \quad (12)$$

and

$$\tau(z) \cong \phi^{-1/3} \quad (13)$$

where ϕ_0 is the surface porosity (taken to be 30%) and K is a scaling factor set by the depth of pore closure (Clifford, 1993).

The subsurface pressure profile is calculated as two extreme values: one that assumes a lithostatic pressure gradient, which would only apply in the case of a negligible subsurface pore space, and one that assumes an atmospheric pressure gradient, which implies an open pore space and unobstructed flow of gas. The real profile will be a complex one that lies somewhere between these two extremes but they are used here as end-member cases.

3. Modelling methane release

The updated model is first applied to the same MCH destabilisation scenarios as in Stevens et al. (2015), which ruled out sources deeper than the MCH stability zone being able to produce transient plumes in the atmosphere at timescales as observed by Mumma et al. (2009) and Webster et al. (2014), in order to calculate the approximate timescales of release and investigate how transient atmospheric methane ‘plumes’ could be created by release from MCH deposits. The amount of methane injected during an event is estimated from the maximum possible production due to serpentinisation, which is $2.9 \times 10^{-5} \text{ kg m}^{-3}$, and a continuous rate under ideal conditions of $1.07 \times 10^{-17} \text{ kg s}^{-1} \text{ m}^{-3}$ which is of the same order of magnitude as release from MCH (Stevens et al., 2015) or biological production (Onstott et al., 2006).

Additional erosion scenarios are also presented, and the model is then applied to determine the change in isotopic composition that will occur in these scenarios.

3.1. Timescales

Table 1 shows the ‘time to surface’ for a number of scenarios, defined by the time taken to reach a concentration of $10^{-11} \text{ kg m}^{-3}$ (approximately 1 ppbv in the martian atmosphere) in the top-most layer of the subsurface, chosen to match observations from the Mars Science Laboratory (Webster et al., 2014). Each scenario either injects a point mass of $2.9 \times 10^{-5} \text{ kg}$ of methane at $t = 0$ or a continuous production rate of $10^{-17} \text{ kg m}^{-3} \text{ s}^{-1}$ at a given depth under a given subsurface pressure gradient. Both values are calculated from estimates of the maximum theoretical production

Table 1

Estimates of how long methane takes to reach the surface for a range of given parameters (in Mars-years). Estimates for the ADM model are taken from Stevens et al. (2015). The $10^{-11} \text{ kg m}^{-3}$ criterion is not met at any point for release at 5 km in the lithostatic case unless constant production is included.

Pressure gradient		Atmospheric		Lithostatic	
Source depth / km		2	5	2	5
ADM model	Zero production rate	1.25	13.4	23,800	719,000
	Production rate $10^{-17} \text{ kg m}^{-3} \text{ s}^{-1}$	1.25	13.3	23,500	665,000
This study	Zero production rate	400,000	3270,000	770,000	–
	Production rate $10^{-17} \text{ kg m}^{-3} \text{ s}^{-1}$	307,000	1960,000	458,000	3340,000

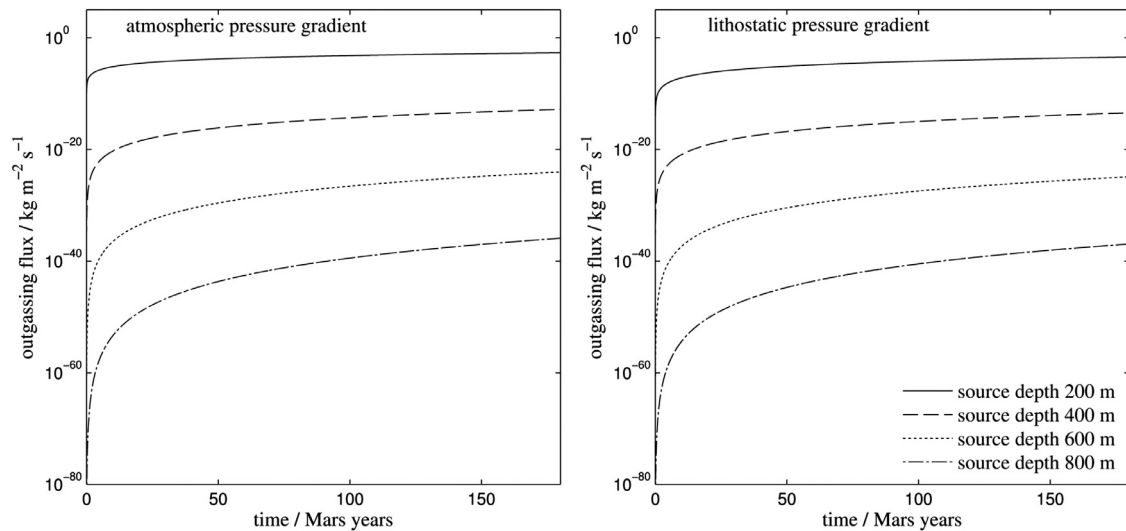


Fig. 1. The outgassing flux due to seasonal erosion destabilising MCH at a depth of between 200 and 800 m in the case of an atmospheric pressure profile. The logarithmic scale highlights that the flux from sources below 200 m is very low throughout the release period.

from serpentinisation of mafic rock. Comparing these to the previously calculated values for the same scenarios (also shown in Table 1), transport timescales are far longer than those calculated for the ADM model in Stevens et al. (2015). The results shown in Table 1 suggest that if the DGM is a more accurate description of gas transport through low permeability porous media, then it will take far longer than previously implied for a source deep ($> 2 \text{ km}$) in the subsurface to release methane into the atmosphere (Stevens et al., 2015), up to several million years from depths of only 5 km.

3.2. Release scenarios

To investigate the possibility of transient release process that can match current observations of sub-annual variability, the destabilisation of MCH deposits by seasonally variable periods of erosion or mass-wasting events was also modelled. Estimates of erosion consistent with the formation of Nilus Mensae at 2 mm a^{-1} (Williams et al., 2000) and mass wasting rates comparable with gully slips of several thousand cubic metres of material similar to those observed from orbit (Dundas et al., 2015), which could destabilise 60 m of MCH in the subsurface in a single event, are the same as those used in Stevens et al. (2015) in order to provide a quantified comparison of the additional mechanisms included in the DGM. Both assume a MCH layer 90% saturated with methane (Max and Clifford, 2000). However, given that continuous erosion has already been shown by Stevens et al. (2015) to be unable to produce a temporally variable flux of methane into the atmosphere, a higher value 'seasonal' erosion rate (of 4 mm a^{-1}) is included that is active for half a martian year. This seasonal destabilisation of MCH could be caused by a number of mechanisms, such as aeolian transport (Ayoub et al., 2014) or CO_2 sublimation

(Hansen et al., 2011), but a full treatment is beyond the scope of this study. A selection of results is shown for this scenario in Fig. 1 for both the atmospheric and lithostatic pressure case.

3.2.1. Erosion

For simulations using the erosion scenario described above, the upward flux of methane through a unit area at the surface (hereafter 'outgassing flux') gradually increases over time. For sources deeper than 200 m the flux does not, however, reach a level of $10^{-14} \text{ kg m}^{-2} \text{ s}^{-1}$ required to match the observations by Mumma et al. (2009) of a release rate of $\geq 0.63 \text{ kg s}^{-1}$ over a plume area of $9.7 \times 10^6 \text{ km}^2$, and in fact is several orders of magnitude below this. The outgassing flux is so low that it is never able to build up, so there is no significant temporal variability evident in the outgassing flux except for the initial increase and approaches a steady state over long timescales of regular seasonal release. There is only a minor difference between the atmospheric and lithostatic pressure gradient cases, and in general the atmospheric pressure gradient case shows a slightly higher outgassing flux.

3.2.2. Mass wasting

The results shown above imply that seasonal cycles of erosion that could destabilise MCH deposits are unable to reproduce observations of methane in the martian atmosphere, agreeing with results described by Stevens et al. (2015). Release caused by mass wasting events was also simulated here to see if it is still compatible with observations when Knudsen diffusion is included. The mass-wasting event simulated here is assumed to move a total mass of $17.6 \times 10^6 \text{ kg}$ over an area of 100 m^2 , destabilising 60 m of MCH.

In this scenario, using the DGM model, the outgassing flux looks very similar to the case of variable erosion, as shown

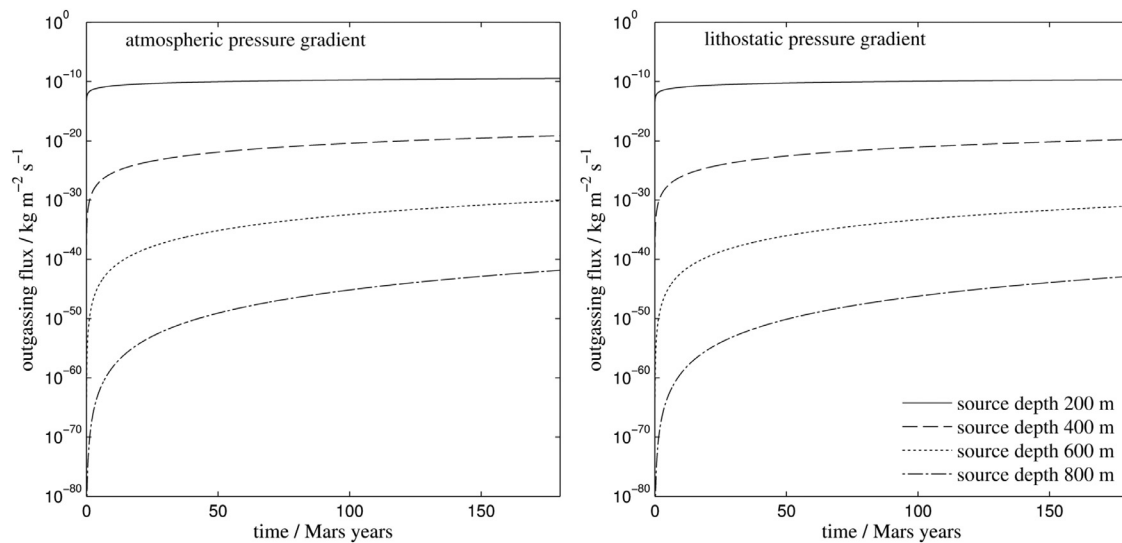


Fig. 2. The outgassing flux due to mass wasting events destabilising MCH at a depth of between 200 and 800 m in the case of an atmospheric pressure profile. Shallower sources produce similar curves at marginally higher outgassing flux.

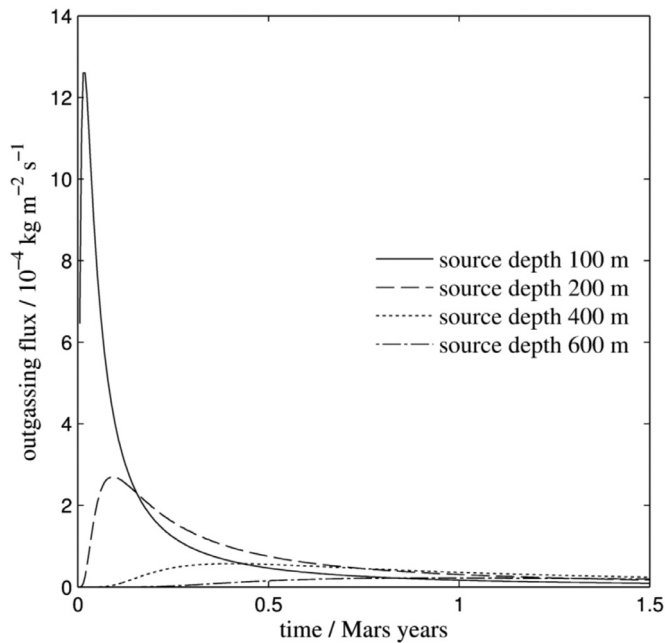


Fig. 3. Comparable release using the same parameters as Fig. 2, using a purely Fickian diffusive model.

in Fig. 2. Sources shallower than around 400 m are capable of reproducing fluxes of 10^{-14} kg m⁻² s⁻¹ consistent with Mumma et al. (2009), but even then no temporal variation is apparent after the initial increase. Instead, the outgassing flux gradually increases over time, and is therefore not consistent with methane ‘plumes’ with a lifetime in the order of martian years – these results suggest that even instantaneous release from a point source produces a flux at the surfaces that varies over periods of several hundred martian years. This is a direct contradiction of previous modelling (with only Fickian diffusion) by Stevens et al. (2015), which showed an appreciable rise and fall in outgassing flux from the same initial scenario (Fig. 3).

The use of the DGM model and incorporation of Knudsen diffusion, which occurs at a rate several orders of magnitude lower than purely Fickian diffusion, shows that the scenarios described

by Stevens et al. (2015) are unlikely to have generated relatively short-lived increases in methane concentration in the martian atmosphere as transport in the subsurface is simply too slow for temporally variable release to be visible at the surface.

4. Change in isotopic composition due to transport

While observations of methane release that varies significantly over short timescales would suggest either a very shallow source or a transport mechanism more rapid than diffusion, information on the source depth could be provided by measuring the isotopic composition of the gas. Modelling the effect of transport on isotopic fractionation can be combined with potential source fractionation values to place constraints on the depth of the methane source by measuring the isotopic composition in the atmosphere. While Section 3 suggests that temporally variable release can only be achieved by transport processes other than pure diffusion, modelling the effect on fractionation due to diffusive transport provides a baseline from which to base estimates of the effect from other mechanisms. Another issue is the unknown nature of Mars’ primordial carbon (Grady et al., 2004) and hydrogen (Greenwood et al., 2008) reservoirs, which means that only relative changes in isotopic composition can be considered, using terrestrial analogues to estimate initial composition.

As shown in Table 1, the timescales of release from methane sources are sensitive to the depth of the source. To investigate how the source depth affects the resulting isotopic composition as it is released into the atmosphere, a series of methane sources with a constant production rate at the source were used as initial conditions for the model while the subsurface porosity, pressure and temperature profiles, the source depth and the initial fractionation of the source were all varied to show how sensitive the change in composition is to each of these properties.

Porosity was found to have only a very small effect upon fractionation. Little variation was found in the measured surface composition of methane for sources at a range of depths over a plausible range of surface porosity values, which sets the porosity profile throughout the regolith column via the relationship described in Eq. 12. There was only a 1% difference between simulations for surface porosities of 20 and 50%, the extremes of values measured by surface instruments to date (Kieffer et al., 1992). Further results

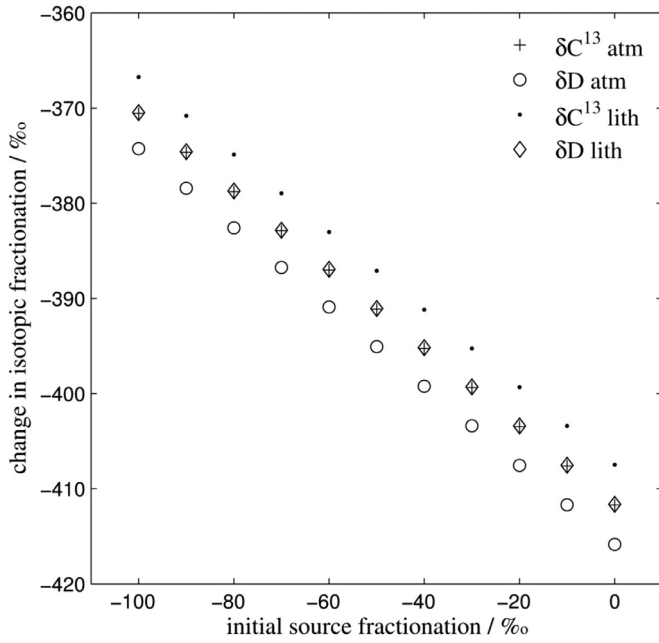


Fig. 4. How the observed surface isotopic composition varies according to changes in the initial source composition for an example source at 200 m.

are all presented with a surface porosity of 30 %, which is a commonly used value between these extremes.

4.1. Effect of source composition

The isotopic composition of the original source was varied to investigate its effect on the observed surface composition, and examples of the results are shown in Fig. 4. There is a linear trend in the variation between observed composition and source composition. This means that from two sources at the same depth but with different initial composition, the observed isotopic composition at the surface would be shifted by a different amount. This is as expected, because changing the initial composition is equivalent to changing the relative concentrations of the different isotopologues at the source, and because the transport rate is dependent on the source concentration, this changes the relative transport rate of the different isotopologues. The linear relationship in the predicted change in composition is due to the formulation of the

model – each isotopologue is treated as a separate, non-interacting trace species travelling through the carrier gas, and so the influence of their relative concentrations is exaggerated. In reality each species will interact, but given the low relative concentration of isotopologues the mutual diffusion coefficient (e.g. $D_{\text{CH}_4-^{13}\text{CH}_4}$) will be very small, especially in the case of a trace gas, and so the effect should be negligible, but fully modelling multicomponent gas diffusion is beyond the scope of this study.

4.2. Effect of pressure

In the DGM model the subsurface pressure profile has a less pronounced effect than the ADM model on the rate of transport, and subsequently the measured fractionation. The case for a point release (of the same type as the mass wasting scenarios described in Section 3.2.2) is shown in Fig. 5. After this point release the observed isotopic composition at the surface stays approximately constant, with a slight increase over time as the heavier isotopologues “catch up”. The isotopic composition measured at the surface shows a large shift from the initial source composition, in this case, for release from 200 m, of around -420 ‰. The shift in composition for the two different isotopologues is different, due to the slight difference in molecular mass between the two. There is negligible difference between the two pressure profile cases, and these are therefore assumed to produce the same results (confirmed in Fig. 7).

4.3. Effect of temperature

The effect of the temperature gradient on the measured surface composition is shown in Fig. 6. Values for a putative modern temperature gradient of 10 K km^{-1} and an ancient martian gradient of 20 K km^{-1} following Michalski et al. (2013) were supplemented by more extreme gradients of $30 - 50 \text{ K km}^{-1}$, but the variation in the shift in composition is less than 1 ‰ for all cases, and the effect of temperature is therefore assumed to be negligible.

4.4. Effect of source depth

The relationship between the depth of the source and the change in the isotopic composition is exponential (Fig. 7). This means that observations of methane release taken at the surface will show a large isotopic depletion compared to the original source composition, and the observed composition will be more depleted if the source is deeper, with sources at around 1 km depth

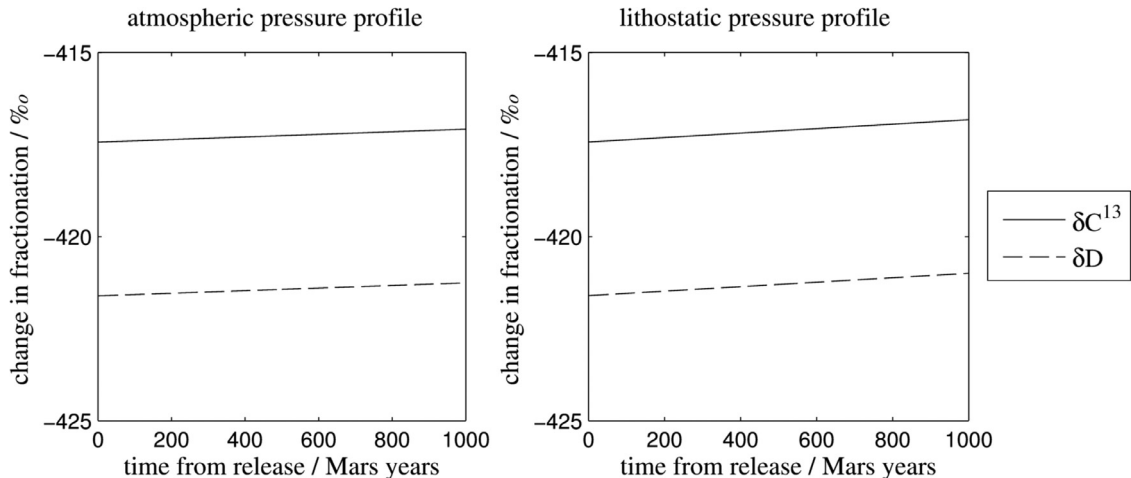


Fig. 5. Isotopic composition measured at the surface after a point release of methane with an initial source composition of 0 ‰ at 200 m depth. These show that there is no apparent difference between the subsurface pressure profiles.

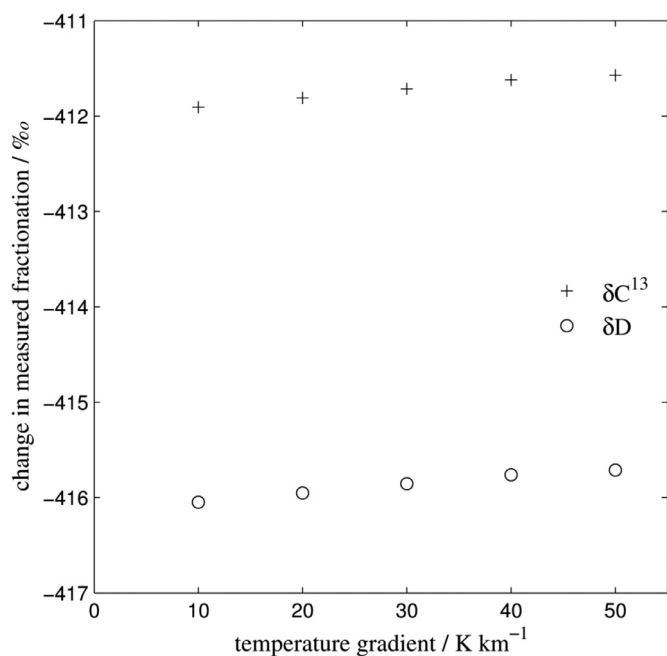


Fig. 6. The effect of subsurface temperature gradient on the alteration of isotopic composition during transport from a source at 200 m depth. δC^{13} and δD are only different by less than 1 ‰.

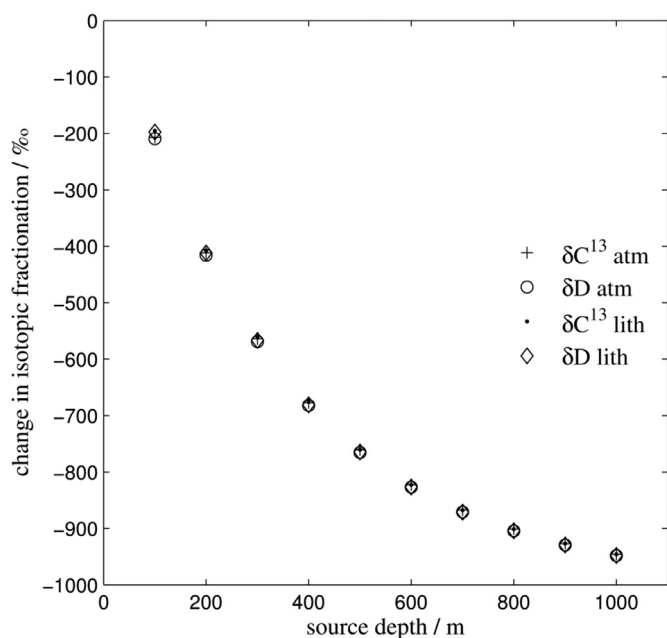


Fig. 7. How the depth of an unfractionated source affects the observed isotopic composition at the surface.

showing a very large change in composition of up to around -950 ‰ (the maximum being -1000 ‰, which is only true if there are no heavier isotopes measured).

This means that, for example, a biogenic source at 500 m depth, with a source composition of -100 ‰, would present the same atmospheric signature as an unfractionated, abiogenic source from a depth of around 800 m. Given the range of potential biogenic and abiogenic isotopic signatures, which can be around 50 ‰ in $\delta^{13}C$ and several hundred parts per mille in δD (Schoell, 1988; Horita and Berndt, 1999; Etiope et al., 2013), a large isotopic depletion could be caused by a biogenic source at moderate depth,

an abiogenic source at extreme depth, or a combination of the two. Measuring a small isotopic depletion would imply that the source was abiogenic and shallow, since the upper layers of the martian subsurface are thought to be uninhabitable. Combining this uncertainty with the unconstrained nature of the martian hydro- and cryo-sphere, more detailed measurements of martian subsurface conditions will be required before a methane source can be conclusively inferred *via* isotopic fractionation measurements alone. Measurements of higher alkanes released with methane and correlation with other released gases may be required to help identify the source (Onstott et al., 2006).

5. Conclusions

A transport model that includes the effect of Knudsen diffusion (which is likely to occur in the low permeability martian regolith) produces transport that is several hundred thousands of years longer than predicted from Fickian diffusion alone. The slower transport generated by Knudsen diffusion means that timescales of methane release from realistic source depths are several hundred thousands of years longer when only considering Fickian diffusion. This increased transport timescale means that any temporal variation in sources, even at shallow depths, is completely damped by diffusive transport in the subsurface, meaning that processes such as methane clathrate hydrate destabilisation caused by seasonally varying erosion or mass-wasting events are not compatible with current observations of 'plumes' of methane in the martian atmosphere without invoking some unknown and relatively fast-acting removal processes such as biological oxidation. Given that abiotic release on Earth is associated with serpentinisation-induced fracturing, fault zones could be a promising place to search for rapid release of methane on Mars.

Simulations using the gas transport model described here show that transport of methane from a subsurface source to the atmosphere will significantly fractionate the methane, potentially disguising any isotopic signatures that would help with identification of the source. Given that the change in isotopic composition is so large, even for sources at shallow depths, this would mean that any biogenic sources, which would likely have a moderately negative $\delta^{13}C$, would be indistinguishable from methane produced deeper by other processes.

The potential influence of sequestration in MCHs complicates the story of transport somewhat. However, since any methane stored in hydrate deposits would have been generated from another source with a typical fractionation and clathrate hydrates have been shown not to significantly fractionate the guest gas incorporated in them (Hachikubo et al., 2007), MCH deposits could be considered in this context simply as a 'buffer' that slows the release from the source but does not affect the change in isotopic composition, though the composition could already have been altered if there were variations in the transport of the methane that formed the MCH. The methane still needs to be transported from the source to the clathrate forming region and from there to the atmosphere.

The fact that isotopic fractionation of gases can be affected by transport or other processes means that identification of the sources of trace gases cannot be achieved by observing the isotopic composition alone. Given that the isotopic phase spaces of different sources of methane overlap significantly and can be altered before observation means that to constrain the original source of methane, multiple lines of evidence must be used. One measurement (e.g. $\delta^{13}C$) pointing towards a biogenic source is not enough to conclusively say that the methane is biogenic, or *vice-versa*. The only inference that can be made from measurement of methane fractionation alone is that if the measured isotopic composition is

close to zero or positive, the source must have been abiotic and shallow, or transported at a significant rate through the subsurface.

Future missions must aim to characterise as many properties of the gas as possible, as well as detecting other associated species. Orbiting spectrometers, such as those that will be launched on the ExoMars Trace Gas Orbiter, should be able to detect and characterise a number of important atmospheric species, including the isotopologues of methane, ethane and butane. Orbital spectroscopy can map the distribution of such gases and therefore point towards the potential source location, but more sensitive *in situ* techniques, such as the Tunable Laser Spectrometer on the Curiosity rover (Webster and Mahaffy, 2011) or cavity ring-down spectrometers (Onstott et al., 2006) might be required to measure the isotopic fractionation of methane and other hydrocarbons to the sensitivity that would be required to comprehensively identify the source, especially as a highly negative isotopic signature would require very high sensitivity to measure since this implies the concentration of heavier isotopologues is very low.

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